The Ion O^- in the Hartree–Fock Approximation

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Summary It is shown that the conventional symmetry constraints generate a spurious solution of the Hartree–Fock equations for the oxygen anion.

In an earlier publication[1] it has been noted that the 'symmetry' restrictions on the solutions of the single-determinant ['Hartree–Fock' (HF)] model of atomic structure produce spurious solutions to the equations and some of the details of the effects of the removal of these constraints were given. In the theory of atoms and atomic ions these restrictions take three main forms. (i) The 'spherical approximation:' the (unfounded) assumption that the atomic HF equations separate into radial and angular equations. (ii) The 'equivalence restriction:' the assumption that the radial function of all orbitals of a given l are the same. (iii) The 'spin eigenfunction' constraint. These restrictions only become really important when dealing with weakly bound electrons. The dominance of the attractive potential of the nucleus is usually such that the constraints are satisfied by the contingencies of the individual case. In this note we report some calculations on the (putative) oxygen negative ion which give a startlingly clear demonstration of the effect of the constraints when one electron is only weakly bound in the experimental system.

If we carry through the finite-basis expansion method of solving the atomic HF equation [with restrictions (i)—(iii)] for O^-, then we can obtain 'HF energies and orbitals' for this system, as, for example, listed in Clementi's tables.[2] The existence of the solutions is never in doubt as the optimisation of both linear and non-linear parameters occurs smoothly and their existence is not dependent on the finite expansion method, as confirmed by the numerical solution of the atomic HF radial equation. However, the energy given by the resulting calculation is above that of the 'parent' atom, oxygen. Thus, the constraints conspire to prevent the equations generating a wave-function for the HF ground state of the system of an oxygen nucleus and 9 electrons; namely an oxygen atom and a free electron.

One obvious apparent limitation of the finite-basis expansion method in this context is the lack of any basis functions which are appropriate to a description of a free electron: Bessel functions in the spherical approximation. However, this is not the source of the difficulty. The problem is that all five of the 'p electrons' are constrained to have the same radial function and so the ion (in the restricted HF case here) *cannot* lose one electron; it must retain all five *or* lose all five and, since the bogus O^- solution has a lower energy than O^{4+}, the ion is predicted 'stable' but with higher energy than the atom. Here we show that it is possible, *even within the symmetry-restricted* HF approach, to show that the negative ion solutions do not exist.

The obvious solution to the equivalence restriction in O^- is to go to an 'excited state' of the ion in which *an electron has its own individual radial function.* There are many such, the formally lowest ones being $1s^2\ 2s^2\ 2p^4\ 3s\ (^6P)$ or $1s^2\ 2s^2\ 2p^4\ 3d(^4F)$. If now a calculation is performed using the finite-basis expansion method with optimised exponents for all basis functions (including the 3s and 3d), the calculation occurs smoothly until the 3s (or 3d) exponents reach zero (or at least the pre-set minimum value) and the 1s, 2s, and 2p functions take on the oxygen atom values. Clearly the trick of giving the 'excited state' function the capacity of losing an electron by indefinite expansion of the 'outer orbital' has simulated ionisation. The optimised $1s^2\ 2s^2\ 2p^4\ 3s\ (^6P)$ 'excited state' function has a lower energy than the $1s^2\ 2s^2\ 2p^5\ (^2P)$ 'ground state.' This establishes conclusively that the restrictions generate the bogus 'ground state' solutions: the same principle applies to O^{2-} and higher ions, of course.

These features should appear in a more direct manner if the constraints (i)—(iii) are removed and the genuine HF equations are solved: one would hope that the optimisation of five *separate* 2p-type functions would show a similar phenomenon: the expansion of one function to the limit of allowed orbital exponents. This is certainly what happens in the case of H$^-$, where a wave function consisting of a single determinant of 1s 1s′ quickly converges to a hydrogen atom solution plus a very diffuse orbital, the whole system having an energy of $-0{\cdot}5E_h$.[3]

For technical reasons the finite expansion method with a *limited* basis was used to test this last hypothesis: a 'double-zeta type' with two-STO radial functions for each of the 1s, 2s, and three 2p orbitals. Optimisation of this basis led to a suprising result: the O$^-$ ion appears stable, *i.e.* the calculation did *not* generate a diffuse orbital and an oxygen atom solution. However, the energy was still above that of the oxygen atom solution. With hindsight, and the knowledge that this solution *must* be bogus, the reason for the discrepancy is clear. In contrast to the added 3s or 3d function in the restricted case, the 2p function of the 'double-zeta' basis is an essential factor in the description of the ion or atom: removal of a basis function by 'ionisation' is a critical factor when the basis size is limited. Thus, in the unrestricted double-zeta case there are two competing effects in the calculation, one of which is a physical effect and the other purely an artefact of the mathematical method used. (a) The energy lowering, resulting from loss of an *electron* from O$^-$. (b) The energy raising, resulting from loss of a *basis function* from a calculation on O. Only in the case that the basis is redundant (or contains functions of higher angular momentum) will (b) be eliminated, allowing the real *physical effect* (a) to operate unhindered.

This is easily confirmed by increasing the basis-set size or by using an 'unlikely' orbital of a diffuse nature in the calculation 4s, 5g, *etc.*: optimisation quickly leads to simulated ionisation as a singly occupied orbital becomes very diffuse.

The conclusions here are obvious for the O$^-$ ion but some more general conclusions concerning the nature of the HF method and, in particular, the real nature of the so-called independent particle model can be drawn. (a) Symmetry restrictions *and* the length of a finite-basis expansion can have *qualitative* effects on the results of a single determinant calculation: in particular both can generate bogus 'solutions' to the HF equations. (b) The independent particle model is only reliable if each electron has a separately optimised orbital *independent of the orbitals of the other electrons* in the system (that is, independent in the sense of unconstrained not, of course, independent of the averaged inter-electron repulsion).

Many of the worst pitfalls of replacing the variational energy function (1) by the paramaterised energy function

$$E = \int \mathrm{d}V\phi^*\mathrm{H}\phi / \int \mathrm{d}V\phi^*\phi \qquad (1)$$

(when ϕ is chosen to depend on the parameters) can be avoided by always using a single-determinant of independently optimised orbitals: symmetries will always emerge if they are relevant.

On a point of terminology, it is perhaps pointless to become involved in an attempt to define what is meant by the term 'Hartree–Fock' since usage (or rather abusage) is so diffuse and varied. The term 'independent-particle model' is, perhaps, the best since it lends itself to stressing the variational optimisation of each particle's distribution independently of the forms of all others; while the term 'single-determinant model' is the most precise.

For neutral systems there is a proof that the solutions of the single-determinant model exist[4] and so computational work can be carried out with some confidence. However, for negative ions, there is no such proof and so actual calculations must always contain an element of exploration and must be done in full generality if any reliance is to be placed on even the qualitative results.[5]

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[1] D. B. Cook, *Theor. Chim. Acta*, submitted for publication.

[2] E. Clementi, Supplement to *IBM J. Res. Dev.*, 1965, **9**, 2.

[3] See, for example, B. Kockel, *Z. Natforsch.*, 1961, **10**, 1021; H. Schull and P. O. Löwdin, *J. Chem. Phys.*, 1956, **25**, 1035; and a recent numerical treatment, B. C. Webster, M. J. Jamieson, and R. F. Stewart, *Adv. At. Mol. Phys.*, 1978, **14**, 87.

[4] E. H. Lieb and B. Simon, *J. Chem. Phys.*, 1965, **61**, 735.

[5] The necessity of using diffuse orbitals in the study of anions is known on an empirical basis: B. C. Webster, *J. Phys. Chem.*, 1975, **79**, 2809; D. M. Chipman, *J. Phys. Chem.*, 1978, **82**, 1080.